JC02 Rec'd PCT/PTO 23 JAN 2001

FORM PTO-1390 (REV 12-29-99) U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER	Mo-6115/LeA 33,123
U S APPLICATION NO-(If known, see 37 CFR 1 5)	To be Assigned 09/744357

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP99/05150	20 July 1999 (20.07.99)	31 July 1998 (31.07.98)

TITLE OF INVENTION BIMETALLIC-CYANIDE CATALYSTS USED FOR PREPARING POLYETHER POLYOLS

APPLICANT(S) FOR DO/EO/US 1) Pieter Ooms; 2) Jorg Hofmann; 3) Pramod Gupta; 4) Walter Schafer

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [X] This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. [X] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [X] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] has been transmitted by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [X] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [X] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [X] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST preliminary amendment.
    [ ] A SECOND or SUBSEQUENT preliminary amendment.
14. [ ] A substitute specification.
15. [ ] A change of power of attorney and/or address letter.
16. [X] Other items or information:

Preliminary Amendment w/Abstract.

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U.S. APPLICATION NO (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
To be Assigned 09/744357	PCT/EP99/05150	Mo-6115/LeA 33,123

17. [X] The following fees are submitted:

	CALCULATIONS	PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO .... **$970.00** International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO....... **$840.00** International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO .... **$690.00** International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) .... **$670.00** International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) **$96.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	13 - 20 =	0	X **$18.00**	$ 0.00	
Independent claims	2 - 3 =	0	X **$78.00**	$ 0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$260.00**	$ 0.00	
TOTAL OF ABOVE CALCULATIONS =				$ 860.00	
Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also by filed (Note 37 CFR 1.9, 1.27, 1.28).				$ 0.00	
SUBTOTAL =				$ 860.00	
Processing fee of **$130.00** for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$	
TOTAL NATIONAL FEE =				$ 860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$ 40.00	
TOTAL FEES ENCLOSED =				$ 900.00	
				Amount to be refunded:	$
				charged:	$

a. [ ] A check in the amount of $________ to cover the above fees is enclosed.

b. [X] Please charge my Deposit Account No. 13-3848 in the amount of $900.00 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO.

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00157
PATENT TRADEMARK OFFICE

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NAME

44,339
REGISTRATION NUMBER

09/744357

JC07 Rec'd PCT/PTO 23 JAN 2001

PATENT APPLICATION
Mo 6115
LeA 33,123

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
PETER OOMS ET AL)
SERIAL NUMBER: TO BE ASSIGNED)
FILED: HEREWITH)
TITLE: BIMETALLIC-CYANIDE CATALYSTS USED FOR PREPARING POLYETHER POLYOLS)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Please enter the following amendments and consider the following remarks in support of the enclosed application:

IN THE TITLE

On page 1, line 1, please delete the words "Double metal cyanide catalysts for the preparation of polyols" and insert therein --BIMETALLLIC-CYANIDE CATALYSTS USED FOR PREPARING POLYETHER POLYOLS --.

IN THE ABSTRACT

In the Abstract, please delete the title which reads "Double metal cyanide catalysts for the preparation of polyols" and insert therein --BIMETALLLIC-CYANIDE CATALYSTS USED FOR PREPARING POLYETHER POLYOLS --.

"Express Mail" mailing label number EL062670805US

Date of Deposit January 23, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch
(Name of person mailing paper or fee)

Donna J. Veatch
(Signature of person mailing paper or fee)

IN THE CLAIMS

Please cancel Claims 1-10.

Please add the following Claims 11-23:

--11. A double-metal cyanide catalyst comprising:

a) at least one double-metal cyanide compound;

b) at least one organic complex ligand which is not a glycidyl ether; and

c) at least one or more glycidyl ethers.

12. The double-metal cyanide catalyst according to Claim 11, further comprising water and/or one or more water-soluble metal salts.

13. The double-metal cyanide catalyst according to Claim 11, wherein the double-metal cyanide compound is of the general formula:

$M_x[M'_{x'}(CN)_y]_z$

14. The double-metal cyanide catalyst according to Claim 13, wherein the double-metal cyanide compound is zinc hexacyanocobaltate (III).

15. The double-metal cyanide catalyst according to Claim 11, wherein the organic complex ligand comprises alcohols, aldehydes, ketones, ethers, esters, amides, ureas, nitriles, sulfides and/or mixtures thereof.

16. The double-metal cyanide catalyst according to Claim 15, wherein the organic complex ligand is tert.-butanol.

17. The double-metal cyanide catalyst according to Claim 11, wherein the glycidyl ether is present in an amount of from about 5 to about 80 wt. % based on the amount of finished double-metal cyanide catalyst.

18. The double-metal cyanide catalyst according to Claim 11, wherein the glycidyl ether is present in an amount of from about 10 to about 60 wt. % based on the amount of finished double-metal cyanide catalyst.

19. The double-metal cyanide catalyst according to Claim 11, wherein the glycidyl ether comprises monomeric or polymeric aliphatic, aromatic or araliphatic, mono-, di-, tri-, tetra- or poly-functional alcohols.

20. The double-metal cyanide catalyst according to Claim 11, wherein the glycidyl ether is a mono- or di-glycidyl ether of butanol, hexanol, octanol, decanol, dodecanol, tetradecanol, ethanediol, or 1,4-butandediol, or is a polypropylene glycol

and/or a polyethylene glycol.

21. The double-metal cyanide catalyst according to Claim 20, wherein the degree of polymerization of the glycidyl ether is from about 2 to about 1000 monomer units.

22. A process for the preparation of double-metal cyanide catalysts according to Claim 11, comprising the steps of reacting: (a) at least one metal salt with at least one metal cyanide salt with at least one glycidyl ether in the presence of an organic complex ligand which is not a glycidyl ether; (b) isolating the catalyst; (c) washing the isolated catalyst; and (d) drying the isolated catalyst.

23. In a process for the production of polyether polyols by polyaddition of alkylene oxides onto starter compounds containing active hydrogen atoms, the improvement wherein said polyaddition of alkylene oxides occurs in the presence of the double-metal cyanide catalyst of Claim 11. --

REMARKS

The amendment to the title of the application and Abstract serves only to place the title in conformance with the title of the PCT application, publication number WO 00/07721. A copy of the amended Abstract page is enclosed for the convenience of the PTO.

Claims 1-10 have been cancelled and rewritten as new Claims 11-23 in an effort to place them in better form.

New Claim 11 corresponds to the subject matter claimed in original Claim 1.

New Claim 12 is directed to the subject matter of original Claim 2.

New Claim 13 is directed to the subject matter of original Claim 3.

New Claim 14 is directed to the subject matter of original Claim 3.

New Claim 15 is directed to the subject matter of original Claim 4.

New Claim 16 is directed to the subject matter of original Claim 4.

New Claim 17 is directed to the subject matter of original Claim 5.

New Claim 18 is directed to the subject matter of original Claim 5.

New Claim 19 is directed to the subject matter of original Claim 6.

New Claim 20 is directed to the subject matter of original Claim 6.

New Claim 21 is directed to the subject matter of original Claim 6.

New Claim 22 is directed to the subject matter of original Claim 7.

New Claim 23 is directed to the subject matter of original Claim 8.

Applicants respectfully submit that no new matter has been added by these amendments. In view of the preceding amendments and remarks, Applicants respectfully request an early action on the merits.

Respectfully submitted,

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BIMETALLLIC-CYANIDE CATALYSTS
USED FOR PREPARING POLYETHER POLYOLS

ABSTRACT OF THE DISCLOSURE

The invention relates to novel double metal cyanide (DMC) catalysts for the preparation of polyether polyols by polyaddition of alkylene oxides to starter compounds containing active hydrogen atoms, wherein the catalyst contains a) double metal cyanide compounds, b) organic complex ligands other than c), and c) complex ligands formed by introduction of a glycidyl ether into the catalyst. The catalysts according to the invention have greatly increased activity in the preparation of polyether polyols.

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Double metal cyanide catalysts for the preparation of polyether polyols

The invention relates to novel double metal cyanide (DMC) catalysts for the preparation of polyether polyols by polyaddition of alkylene oxides to starter compounds containing active hydrogen atoms.

Double metal cyanide (DMC) catalysts for the polyaddition of alkylene oxides to starter compounds containing active hydrogen atoms are known (see, for example, US 3 404 109, US 3 829 505, US 3 941 849 and US 5 158 922). The use of those DMC catalysts for the preparation of polyether polyols brings about in particular a reduction in the proportion of monofunctional polyethers having terminal double bonds, so-called monools, in comparison with the conventional preparation of polyether polyols by means of alkali catalysts, such as alkali hydroxides. The polyether polyols so obtained can be processed to high-quality polyurethanes (e.g. elastomers, foams, coatings). DMC catalysts are usually obtained by reacting an aqueous solution of a metal salt with the aqueous solution of a metal cyanide salt in the presence of an organic complex ligand, for example an ether. In a typical catalyst preparation, for example, aqueous solutions of zinc chloride (in excess) and potassium hexacyanocobaltate are mixed, and dimethoxyethane (glyme) is then added to the suspension formed. After filtration and washing of the catalyst with aqueous glyme solution, an active catalyst of the general formula

$$Zn_3[Co(CN)_6]_2 \bullet x\,ZnCl_2 \bullet yH_2O \bullet z\text{ glyme}$$

is obtained (see, for example, EP 700 949).

From JP 4 145 123, US 5 470 813, EP 700 949, EP 743 093, EP 761 708 and WO 97/40086 there are known DMC catalysts which, by the use of tert.-butanol as organic complex ligand (alone or in combination with a polyether (EP 700 949, EP 761 708, WO 97/40086)), further reduce the proportion of monofunctional

polyethers having terminal double bonds in the preparation of polyether polyols. Moreover, the use of those DMC catalysts reduces the induction time in the polyaddition reaction of the alkylene oxides with appropriate starter compounds and increases the catalyst activity. The use of ligand combinations of tert.-butanol and polyalkylene glycols (e.g. polypropylene glycol) is preferred.

The object of the present invention was to make available further improved DMC catalysts for the polyaddition of alkylene oxides to appropriate starter compounds, which catalysts exhibit increased catalyst activity as compared with the catalyst types known hitherto. By shortening the alkoxylation times, this leads to an improvement in the process for preparing polyether polyols in terms of economy. Ideally, as a result of the increased activity, the catalyst can then be used in such low concentrations (25 ppm or less) that the very expensive separation of the catalyst from the product is no longer necessary and the product can be used directly for the preparation of polyurethanes.

Surprisingly, it has now been found that DMC catalysts that contain a complex ligand formed by introduction of a glycidyl ether into the catalyst possess greatly increased activity in the preparation of polyether polyols.

Accordingly, the present invention provides a double metal cyanide (DMC) catalyst containing

a) one or more, preferably one, double metal cyanide compound(s),

b) one or more, preferably one, organic complex ligand(s) other than c), and

c) one or more, preferably one, complex ligand(s) formed by introduction of a glycidyl ether into the catalyst.

The catalyst according to the invention may optionally contain d) water, preferably from 1 to 10 wt.%, and/or e) one or more water-soluble metal salts, preferably from 5 to 25 wt.%, of formula (I) $M(X)_n$ from the preparation of the double metal cyanide compounds a). In formula (I), M is selected from the metals Zn(II), Fe(II), Ni(II), Mn(II), Co(II), Sn(II), Pb(II), Fe(III), Mo(IV), Mo(VI), Al(III), V(V), V(IV), Sr(II), W(IV), W(VI), Cu(II) and Cr(III). Zn(II), Fe(II), Co(II) and Ni(II) are especially preferred. The substituents X are identical or different, preferably identical, and represent an anion, preferably selected from the group of the halides, hydroxides, sulfates, carbonates, cyanates, thiocyanates, isocyanates, isothiocyanates, carboxylates, oxalates and nitrates. The value of n is 1, 2 or 3.

The double metal cyanide compounds a) contained in the catalysts according to the invention are the reaction products of water-soluble metal salts and water-soluble metal cyanide salts.

Water-soluble metal salts suitable for the preparation of double metal cyanide compounds a) preferably have the general formula (I) $M(X)_n$, wherein M is selected from the metals Zn(II), Fe(II), Ni(II), Mn(II), Co(II), Sn(II), Pb(II), Fe(III), Mo(IV), Mo(VI), Al(III), V(V), V(IV), Sr(II), W(IV), W(VI), Cu(II) and Cr(III). Zn(II), Fe(II), Co(II) and Ni(II) are especially preferred. The substituents X are identical or different, preferably identical, and represent an anion, preferably selected from the group of the halides, hydroxides, sulfates, carbonates, cyanates, thiocyanates, isocyanates, isothiocyanates, carboxylates, oxalates and nitrates. The value of n is 1, 2 or 3.

Examples of suitable water-soluble metal salts are zinc chloride, zinc bromide, zinc acetate, zinc acetylacetonate, zinc benzoate, zinc nitrate, iron(II) sulfate, iron(II) bromide, iron(II) chloride, cobalt(II) chloride, cobalt(II) thiocyanate, nickel(II) chloride and nickel(II) nitrate. Mixtures of various water-soluble metal salts may also be used.

Water-soluble metal cyanide salts suitable for the preparation of double metal cyanide compounds a) preferably have the general formula (II) $(Y)_a\, M'(CN)_b\, (A)_c$, wherein M' is selected from the metals Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III), Ir(III), Ni(II), Rh(III), Ru(II), V(IV) and V(V). M' is selected especially from the metals Co(II), Co(III), Fe(II), Fe(III), Cr(III), Ir(III) and Ni(II). The water-soluble metal cyanide salt may contain one or more of those metals. The substituents Y are identical or different, preferably identical, and represent an alkali metal ion or an alkaline earth metal ion. The substituents A are identical or different, preferably identical, and represent an anion selected from the group of the halides, hydroxides, sulfates, carbonates, cyanates, thiocyanates, isocyanates, isothiocyanates, carboxylates, oxalates and nitrates. a as well as b and c are integers, the values for a, b and c being so selected that the metal cyanide salt is electroneutral; a is preferably 1, 2, 3 or 4; b is preferably 4, 5 or 6; c preferably has the value 0. Examples of suitable water-soluble metal cyanide salts are potassium hexacyanocobaltate(III), potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), calcium hexacyanocobaltate(III) and lithium hexacyanocobaltate(III).

Preferred double metal cyanide compounds a) contained in the catalysts according to the invention are compounds of the general formula (III)

$$M_x[M'_{x'}(CN)_y]_z$$

wherein M is as defined in formula (I) and
M' is as defined in formula (II) and
x, x', y and z are integers and are so selected that the double metal cyanide compound has electron neutrality.

Preferably,

x = 3, x' = 1, y = 6 and z = 2,

M = Zn(II), Fe(II), Co(II) or Ni(II) and

M' = Co(III), Fe(III), Cr(III) or Ir(III).

Examples of suitable double metal cyanide compounds a) are zinc hexacyanocobaltate(III), zinc hexacyanoiridate(II), zinc hexacyanoferrate(III) and cobalt(II) hexacyanocobaltate(III). Further examples of suitable double metal cyanide compounds will be found in, for example, US 5 158 922 (column 8, lines 29-66). The use of zinc hexacyanocobaltate(III) is especially preferred.

The organic complex ligands b) contained in the DMC catalysts according to the invention are in principle known and are described in detail in the prior art (see, for example, US 5 158 922, especially column 6, lines 9-65, US 3 404 109, US 3 829 505, US 3 941 849, EP 700 949, EP 761 708, JP 4 145 123, US 5 470 813, EP 743 093 and WO 97/40086). Preferred organic complex ligands are water-soluble organic compounds having hetero atoms, such as oxygen, nitrogen, phosphorus or sulfur, which are able to form complexes with the double metal cyanide compound a). Suitable organic complex ligands are, for example, alcohols, aldehydes, ketones, ethers, esters, amides, ureas, nitriles, sulfides and mixtures thereof. Preferred organic complex ligands are water-soluble aliphatic alcohols, such as ethanol, isopropanol, n-butanol, isobutanol, sec.-butanol and tert.-butanol. Tert.-butanol is especially preferred.

The organic complex ligand is added either during preparation of the catalyst or immediately after precipitation of the double metal cyanide compound a). The organic complex ligand is usually employed in excess.

The DMC catalysts according to the invention contain the double metal cyanide compounds a) in amounts of from 20 to 90 wt.%, preferably from 25 to 80 wt.%,

based on the amount of finished catalyst, and the organic complex ligands b) in amounts of from 0.5 to 30 wt.%, preferably from 1 to 25 wt.%, based on the amount of finished catalyst. The DMC catalysts according to the invention usually contain from 5 to 80 wt.%, preferably from 10 to 60 wt.%, based on the amount of finished catalyst, of complex ligands c) formed by introduction of a glycidyl ether into the catalyst.

There are suitable for the preparation of the catalysts according to the invention, for example, glycidyl ethers of monomeric or polymeric (having at least two monomer units) aliphatic, aromatic or araliphatic, mono-, di-, tri-, tetra- or poly-functional alcohols.

Preference is given to glycidyl ethers of mono-, di-, tri-, tetra- or poly-functional aliphatic alcohols, such as butanol, hexanol, octanol, decanol, dodecanol, tetradecanol, ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, 1,2,3-propanetriol, 1,6-hexanediol, 1,1,1-tris(hydroxymethyl)ethane, 1,1,1-tris(hydroxymethyl)propane, tetrakis(hydroxymethyl)methane, sorbitol, polyethylene glycol and polypropylene glycol, there being suitable mono-, di-, tri- and tetra- as well as poly-ethers.

Special preference is given to the use of mono- or di-glycidyl ethers of butanol, hexanol, octanol, decanol, dodecanol, tetradecanol, ethanediol or 1,4-butanediol, as well as polypropylene glycol or polyethylene glycol, especially having degrees of polymerisation of from 2 to 1000 monomer units.

Any desired mixtures of the above-mentioned glycidyl ethers may also be used.

The glycidyl ethers are generally obtained by reaction of mono-, di-, tri-, tetra- or poly-functional alcohols with epichlorohydrin in the presence of a Lewis acid, such as, for example, tin tetrachloride or boron trifluoride, to form the corresponding

chlorohydrins, and subsequent dehydrohalogenation with a base (e.g. sodium hydroxide).

Methods of preparing glycidyl ethers are generally well known and are described in detail, for example, in "Kirk-Othmer, Encyclopedia of Chemical Technology", Vol. 9, 4th edition, 1994, p. 739 ff and "Ullmann - Encyclopedia of Industrial Chemistry", Vol. A9, 5th edition, Weinheim/New York, 1987, p. 552.
The glycidyl ether used for the preparation of the catalyst according to the invention may be present in the finished catalyst in the form in which it was originally employed or in chemically changed, for example hydrolysed, form.

Analysis of the catalyst composition is usually carried out by means of elemental analysis and thermogravimetry or removal by extraction of the complex ligand formed by introduction of a glycidyl ether into the catalyst, with subsequent gravimetric determination.

The catalysts according to the invention may be crystalline, partially crystalline or amorphous. Analysis of the crystallinity is usually carried out by powder X-ray diffraction.

Preference is given to catalysts according to the invention containing

a) zinc hexacyanocobaltate(III),

b) tert.-butanol and

c) mono- or di-glycidyl ether of butanol, hexanol, octanol, decanol, dodecanol, tetradecanol, ethanediol, 1,4-butanediol, polypropylene glycol or polyethylene glycol.

Preparation of the DMC catalysts according to the invention is usually carried out in aqueous solution by reacting α) metal salts, especially of formula (I), with metal cyanide salts, especially of formula (II), β) organic complex ligands b) other than glycidyl ether, and γ) glycidyl ether.

In the preparation it is preferable first to react the aqueous solutions of the metal salt (e.g. zinc chloride used in stoichiometric excess (at least 50 mol.%, based on the metal cyanide salt)) and of the metal cyanide salt (e.g. potassium hexacyanocobaltate) in the presence of the organic complex ligand b) (e.g. tert.-butanol), there being formed a suspension which contains the double metal cyanide compound a) (e.g. zinc hexacyanocobaltate), water d), excess metal salt e) and the organic complex ligand b).

The organic complex ligand b) may be present in the aqueous solution of the metal salt and/or of the metal cyanide salt, or it is added directly to the suspension obtained after precipitation of the double metal cyanide compound a). It has proved advantageous to mix the aqueous solutions and the organic complex ligand b), with vigorous stirring. The suspension formed is then usually treated with the glycidyl ether. The glycidyl ether is preferably used in a mixture with water and organic complex ligand b).

The catalyst is then isolated from the suspension by known techniques, such as centrifugation or filtration. In a preferred variant, the isolated catalyst is then washed with an aqueous solution of the organic complex ligand b) (e.g. by being re-suspended and subsequently isolated again by filtration or centrifugation). In that manner it is possible to remove, for example, water-soluble by-products, such as potassium chloride, from the catalyst according to the invention.

The amount of organic complex ligand b) in the aqueous washing solution is preferably from 40 to 80 wt.%, based on the total solution. Furthermore, it is

advantageous to add to the aqueous washing solution a small amount of glycidyl ether, preferably in the range of from 0.5 to 5 wt.%, based on the total solution.

It is also advantageous to wash the catalyst more than once. To that end, the first washing procedure may be repeated, for example. It is, however, preferred to use non-aqueous solutions for further washing procedures, for example a mixture of organic complex ligand and glycidyl ether.

The washed catalyst, optionally after pulverisation, is then dried at temperatures of generally from 20 to 100°C and at pressures of generally from 0.1 mbar to normal pressure (1013 mbar).

The present invention relates also to the use of the DMC catalysts according to the invention in a process for the preparation of polyether polyols by polyaddition of alkylene oxides to starter compounds containing active hydrogen atoms.

There are used as alkylene oxides preferably ethylene oxide, propylene oxide, butylene oxide and mixtures thereof. The synthesis of the polyether chains by alkoxylation may be carried out, for example, with only one monomeric epoxide or in a random or block manner with 2 or 3 different monomeric epoxides. Further details will be found in "Ullmanns Encyclopädie der industriellen Chemie", English language edition, 1992, Vol. A21, pages 670-671.

There are preferably used as starter compounds containing active hydrogen atoms compounds having molecular weights of from 18 to 2000 and having from 1 to 8 hydroxyl groups. There may be mentioned by way of example: ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butanediol, hexamethylene glycol, bisphenol A, trimethylolpropane, glycerol, pentaerythritol, sorbitol, cane sugar, decomposed starch or water.

Advantageously, the starter compounds containing active hydrogen atoms that are used are those which have been prepared, for example, by conventional alkali catalysis from the above-mentioned low molecular weight starters and which are oligomeric alkoxylation products having molecular weights of from 200 to 2000.

The polyaddition, catalysed by the catalysts according to the invention, of alkylene oxides to starter compounds containing active hydrogen atoms is generally carried out at temperatures of from 20 to 200°C, preferably in the range of from 40 to 180°C, especially at temperatures of from 50 to 150°C. The reaction may be carried out at total pressures of from 0 to 20 bar. The polyaddition may be carried out without a solvent or in an inert organic solvent, such as toluene and/or THF. The amount of solvent is usually from 10 to 30 wt.%, based on the amount of polyether polyol to be prepared.

The catalyst concentration is so selected that good control of the polyaddition reaction under the given reaction conditions is possible. The catalyst concentration is generally in the range of from 0.0005 wt.% to 1 wt.%, preferably in the range of from 0.001 wt.% to 0.1 wt.%, especially in the range of from 0.001 to 0.0025 wt.%, based on the amount of polyether polyol to be prepared.

The molecular weights of the polyether polyols prepared by the process according to the invention are in the range of from 500 to 100,000 g/mol., preferably in the range of from 1000 to 50,000 g/mol., especially in the range of from 2000 to 20,000 g/mol..

The polyaddition may be carried out continuously or discontinuously, for example in a batch or semi-batch process.

The use of the DMC catalysts according to the invention reduces the alkoxylation times in the preparation of polyether polyols by typically from 70 to 75 %, as

compared with DMC catalysts known hitherto containing tert.-butanol and polyalkylene glycols as ligands. The shortening of the alkoxylation times in the polyether polyol preparation results in an improvement in the process in terms of economy.

On account of their markedly increased activity, the catalysts according to the invention can be used in very low concentrations (25 ppm and below, based on the amount of polyether polyol to be prepared). If the polyether polyols prepared in the presence of the catalysts according to the invention are used for the preparation of polyurethanes (Kunststoffhandbuch, Vol. 7, Polyurethane, 3rd edition, 1993, p. 25-32 and 57-67), it is possible to dispense with removal of the catalyst from the polyether polyol without the product qualities of the resulting polyurethane being adversely affected.

The Examples which follow illustrate the invention but are not intended to be limiting.

Examples

Catalyst preparation

Example 1

Preparation of a DMC catalyst using a polypropylene glycol diglycidyl ether having a number-average molecular weight of 640 (catalyst A).

A solution of 12.5 g (91.5 mmol.) of zinc chloride in 20 ml of distilled water is added, with vigorous stirring (24,000 rpm), to a solution of 4 g (12 mmol.) of potassium hexacyanocobaltate in 70 ml of distilled water. Immediately thereafter, a mixture of 50 g of tert.-butanol and 50 g of distilled water is added to the suspension which has formed, and vigorous stirring is then carried out for 10 minutes (24,000 rpm). A mixture of 1 g of a polypropylene glycol bis(2,3-epoxypropyl ether) having a number-average molecular weight of 640 (Aldrich), 1 g of tert.-butanol and 100 g of distilled water is then added, and stirring is carried out for 3 minutes (1000 rpm). The solid material is isolated by means of filtration, then stirred for 10 minutes (10,000 rpm) with a mixture of 70 g of tert.-butanol, 30 g of distilled water and 1 g of the above polypropylene glycol bis(2,3-epoxypropyl ether), and filtered again. Finally, the mixture is stirred for a further 10 minutes (10,000 rpm) with a mixture of 100 g of tert.-butanol and 0.5 g of the above polypropylene glycol bis(2,3-epoxypropyl ether). After filtration, the catalyst is dried at 50°C and normal pressure until constant weight is reached.

Yield of dry, powdered catalyst: 8.70 g

Elemental analysis, thermogravimetric analysis and extraction:
cobalt = 8.7 %, zinc = 20.2 %, tert.-butanol = 4.2 %, polypropylene glycol diglycidyl ether ligand = 30.5 %

Example 2

Preparation of a DMC catalyst using a polypropylene glycol diglycidyl ether having a number-average molecular weight of 380 (catalyst B).

The procedure of Example 1 was followed, but a polypropylene glycol bis(2,3-epoxypropyl ether) having a number-average molecular weight of 380 (Aldrich) was used as the glycidyl ether instead of the polypropylene glycol bis(2,3-epoxypropyl ether) from Example 1.

Yield of dry, powdered catalyst: 6.40 g

Elemental analysis, thermogravimetric analysis and extraction:
cobalt = 9.1 %, zinc = 22.1 %, tert.-butanol = 2.2 %, polypropylene glycol diglycidyl ether ligand = 37.8 %

Example 3

Preparation of a DMC catalyst using a polyethylene glycol diglycidyl ether having a number-average molecular weight of 3350 (catalyst C).

The procedure of Example 1 was followed, but poly(oxyethylene) bis(glycidyl ether) having a number-average molecular weight of 3350 (Sigma) was used as the glycidyl ether instead of the polypropylene glycol bis(2,3-epoxypropyl ether) from Example 1.

Yield of dry, powdered catalyst: 5.60 g

Elemental analysis, thermogravimetric analysis and extraction:
cobalt = 7.7 %, zinc = 17.6 %, tert.-butanol = 10.0 %, polyethylene glycol diglycidyl ether ligand = 35.6 %

Example 4 (comparison example)

Preparation of a DMC catalyst using a polypropylene glycol having a number-average molecular weight of 420 (catalyst D, synthesis according to WO 97/40086).

A solution of 12.5 g (91.5 mmol.) of zinc chloride in 20 ml of distilled water is added, with vigorous stirring (24,000 rpm), to a solution of 4 g (12 mmol.) of potassium hexacyanocobaltate in 70 ml of distilled water. Immediately thereafter, a mixture of 50 g of tert.-butanol and 50 g of distilled water is added to the suspension which has formed, and vigorous stirring is then carried out for 10 minutes (24,000 rpm). A mixture of 1 g of a polypropylene glycol having a number-average molecular weight of 420, 1 g of tert.-butanol and 100 g of distilled water is then added, and stirring is carried out for 3 minutes (1000 rpm). The solid material is isolated by means of filtration, then stirred for 10 minutes (10,000 rpm) with a mixture of 70 g of tert.-butanol, 30 g of distilled water and 1 g of the above polypropylene glycol, and filtered again. Finally, the mixture is stirred for a further 10 minutes (10,000 rpm) with a mixture of 100 g of tert.-butanol and 0.5 g of the above polypropylene glycol. After filtration, the catalyst is dried at 50°C and normal pressure until constant weight is reached.

Yield of dry, powdered catalyst: 5.7 g

Elemental analysis, thermogravimetric analysis and extraction:
cobalt = 10.1 %, zinc = 23.0 %, tert.-butanol = 6.3 %, polypropylene glycol = 33.3 %

Preparation of polyether polyols

General procedure

50 g of polypropylene glycol starter (molecular weight = 1000 g/mol.) and 3 mg of catalyst (15 ppm, based on the amount of polyether polyol to be prepared) are placed under a protective gas (argon) in a 500 ml pressurised reactor and heated to 105°C, with stirring. Propylene oxide (approximately 5 g) is then metered in in a single batch until the total pressure has risen to 2.5 bar. No further propylene oxide is then metered in until an accelerated pressure drop in the reactor is observed. That accelerated pressure drop indicates that the catalyst is activated (end of the induction time). The remaining propylene oxide (145 g) is then metered in continuously at a constant total pressure of 2.5 bar. When metering in of the propylene oxide is complete and after a subsequent reaction time of 2 hours at 105°C, volatile portions are distilled off at 90°C (1 mbar) and then cooled to room temperature.

The resulting polyether polyols were characterised by determination of the OH numbers, the double bond contents and the viscosities.

The progress of the reaction was monitored by means of time-conversion curves (propylene oxide consumption [g] vs. reaction time [min]). The induction time was determined from the point of intersection of the tangent at the steepest point of the time-conversion curve with the extended base line of the curve. The propoxylation times, which are of decisive importance for the catalyst activity, correspond to the period of time between activation of the catalyst (end of the induction time) and the end of propylene oxide metering.

Example 5

Preparation of polyether polyol using catalyst A (15 ppm)

propoxylation time:		160 min
polyether polyol:	OH number (mg of KOH/g):	30.0
	double bond content (mmol./kg):	7
	viscosity 25°C (mPas):	897

Example 6

Preparation of polyether polyol using catalyst B (15 ppm)

propoxylation time:		190 min
polyether polyol:	OH number (mg of KOH/g):	29.6
	double bond content (mmol./kg):	9
	viscosity 25°C (mPas):	954

Example 7

Preparation of polyether polyol using catalyst C (15 ppm)

propoxylation time:		185 min
polyether polyol:	OH number (mg of KOH/g):	30.4
	double bond content (mmol./kg):	8
	viscosity 25°C (mPas):	839

Example 8 (comparison example)

Preparation of polyether polyol using catalyst D (15 ppm)

propoxylation time:		650 min
polyether polyol:	OH number (mg of KOH/g):	29.0
	double bond content (mmol./kg):	8
	viscosity 25°C (mPas):	967

Patent claims

1. Double metal cyanide (DMC) catalyst containing

   a) one or more double metal cyanide compounds,

   b) one or more organic complex ligands other than c), and

   c) one or more complex ligands formed by introduction of a glycidyl ether into the catalyst.

2. DMC catalyst according to claim 1, additionally containing d) water and/or e) water-soluble metal salt.

3. DMC catalyst according to claim 1 or 2, wherein the double metal cyanide compound is zinc hexacyanocobaltate(III).

4. DMC catalyst according to any one of claims 1 to 3, wherein the organic complex ligand is tert.-butanol.

5. DMC catalyst according to any one of claims 1 to 4, wherein the catalyst contains from 5 to 80 wt.%, preferably from 10 to 60 wt.%, of a complex ligand formed by introduction of a glycidyl ether into the catalyst.

6. DMC catalyst according to any one of claims 1 to 5, wherein the glycidyl ether is derived from an aliphatic alcohol.

7. Process for the preparation of a DMC catalyst according to any one of claims 1 to 6, comprising the steps:

i) reacting in aqueous solution

α) metal salts with metal cyanide salts,

β) organic complex ligands other than glycidyl ether, and

γ) glycidyl ether,

ii) isolating, washing and drying the catalyst obtained in step i).

8. Process for the preparation of polyether polyols by polyaddition of alkylene oxides to starter compounds containing active hydrogen atoms, in the presence of one or more DMC catalysts according to any one of claims 1 to 6.

9. Polyether polyol obtainable by the process according to claim 8.

10. Use of one or more DMC catalysts according to any one of claims 1 to 6 for the preparation of polyether polyols by polyaddition of alkylene oxides to starter compounds containing active hydrogen atoms.

Double metal cyanide catalysts for the preparation of polyether polyols

Abstract

The invention relates to novel double metal cyanide (DMC) catalysts for the preparation of polyether polyols by polyaddition of alkylene oxides to starter compounds containing active hydrogen atoms, wherein the catalyst contains a) double metal cyanide compounds, b) organic complex ligands other than c), and c) complex ligands formed by introduction of a glycidyl ether into the catalyst. The catalysts according to the invention have greatly increased activity in the preparation of polyether polyols.

COMBINED DECLARATION AND POWER OF ATTORNEY	ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought
on the invention entitled

"BIMETALLIC-CYANIDE CATALYSTS USED FOR PREPARING POLYETHER POLYOLS"

the specification of which is attached hereto,

or was filed on **July 20, 1999**

as a PCT Application Serial No. **PCT/EP99/05150**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

198 34 573.9	**Germany**	**July 31, 1998**
(Number)	(Country)	(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occured between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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